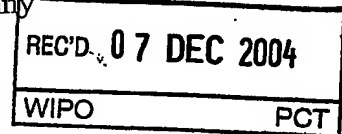Patents Office
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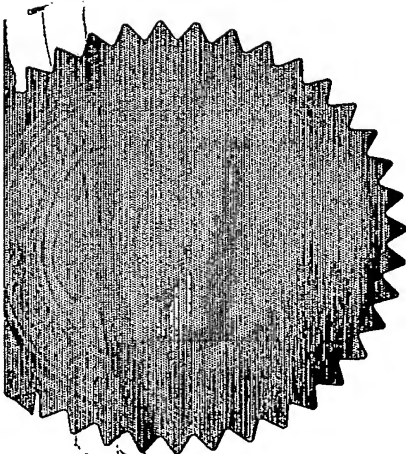|	
Application No.	S2003/0869
Date of Filing	21 November 2003
Applicant	THE NATIONAL UNIVERSITY OF IRELAND, GALWAY, a body corporate, incorporated by Royal Charter as amended by the University Act, 1977 of College Road, Galway, County Galway, Ireland.

Dated this **30** day of November 2004.

An officer authorised by the
Controller of Patents, Designs and Trademarks.

FORM NO. 1

REQUEST FOR THE GRANT OF A PATENT

PATENTS ACT 1992

The Applicant(s) named herein hereby request(s)
    [   ] the grant of a patent under Part II of the Act
    [X] the grant of a short-term patent under Part III of the
Act
on the basis of the information furnished hereunder.

1. Applicant(s)

THE NATIONAL UNIVERSITY OF IRELAND, GALWAY
College Road
Galway
County Galway
Ireland
a body corporate, incorporated by Royal Charter as amended
by the University Act, 1977 of

2. Title of Invention
A soluble metal oxide

3. Declaration of Priority on basis of previously filed
   application(s) for same invention (Sections 25 & 26)

Previous Filing Date	Country in or for which filed	Filing No.

4. Identification of Inventor(s)

   Name(s) and addresse(s) of person(s) believed
   by the Applicant(s) to be the inventor(s)
Patrick Desmond Cunningham
An Irish citizen of Furbo, Spiddal, County Galway, Ireland
James Mc Manus
An Irish citizen of Riverview, Athlone, County Westmeath, Ireland

5. <u>Statement of right to be granted a patent (Section 17(2) (b))</u>

The Applicant derives the right th apply by virtue of a Deed of Assignment Dated November 20, 2003

6. <u>Items accompanying this Request</u>

(i)   [X] prescribed filing fee (Euro 60.00)
(ii) [ ] specification containing a description and claims
      [X] specification containing a description only
      [X] Drawings referred to in description or claims
(iii) [ ] An abstract
(iv) [ ] Copy of previous application(s) whose priority is claimed
(v)   [ ] Translation of previous application whose priority is claimed
(vi) [ ] Authorisation of Agent (this may be given at 8 below if this Request is signed by the Applicant(s))

7. <u>Divisional Application(s)</u>
The following information is applicable to the present application which is made under Section 24 -

Earlier Application No.
      Filing Date:

8. <u>Agent</u>

The following is authorised to act as agent in all proceedings connected with the obtaining of a patent to which this request relates and in relation to any patent granted -
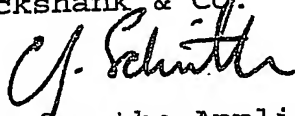
<u>Name & Address</u>

Cruickshank & Co. at their address recorded for the time being in the Register of Patent Agents is hereby appointed Agents and address for service, presently 1 Holles Street, Dublin 2.

9. <u>Address for service (if different from that at 8)</u>

<u>Signed</u> Cruickshank & Co.

By:-   Executive.

Agents for the Applicant

<u>Date November 21, 2003.</u>

"A soluble metal oxide"

The present invention relates to a soluble metal oxide. The invention further relates to a process for preparing a soluble metal oxide.

In the specification the term "metal oxide" refers to a chemical compound in which oxygen is combined with a metal. In the specification the term "particle" refers to a crystalline structure having a diameter of less than 50Å.

Metal oxides and in particular tin oxide have an important role in many coating applications:

(a)   Domestic glassware and bottles contain a thin coating of tin oxide to greatly enhance impact resistance. Thicker coatings confer iridescent appearances that provide attractive finishes to glass objects.

(b)   Thin coatings of tin oxide on window glass serve to reflect indoor heat inwards in winter time and reduce solar heating in summer time.

(c)   Conducting tin oxide films have a vital role as transparent electrodes in the construction of many important devices including light harvesting solar cells, electrochromic cells and liquid crystal displays. Conducting tin oxide films can also be applied to car and aircraft windscreens.

(d)   Thin coatings of tin oxide are used to improve bonding characteristics of surfaces. A coating of tin oxide on alumina can be used to enhance bonding for high-alumina dental ceramics.

(e)   Tin oxide films can be used in many applications and industries as gas sensors.

(f)   Metal oxide coatings reduce surface friction and thus have applications for moving parts in engines.

Metal oxides coatings also have important roles in other applications such as use in the production of industrial catalysts. In such applications, the catalyst fabrication process is vitally important for catalytic performance.

5   Current methods for the preparation of metal oxide coatings from metal oxide include:

a)   Vacuum techniques such as Chemical Vapour Deposition (CVD), electron-beam evaporation and reactive sputtering. Chemical Vapour Deposition is the growth of thin solid films as the result of thermo-chemical vapour-phase reactions. This technique requires however specialised equipment and the use

10   of suitable volatile metal precursors. Furthermore, there is an associated high cost of maintaining the high vacuum required and the precise heating control to vaporise the precursor material.

15   b)   Pyrolysis/hydrolysis of the vapour of a suitable metal compound on a hot substrate surface. In the case of tin coating of glassware this technique requires the use of tin tetrachloride and butyltin trichloride as precursors. Tin tetrachloride is a highly corrosive caustic liquid which can be irritating to the user. Both compounds produce corrosive hydrogen chloride gas during the

20   hydrolysis and subsequent formation of tin oxide films.

c)   In the sol-gel technique a suitable precursor undergoes slow hydrolysis to give the sol. Evaporation of the solvent produces the gel. The precursor is often a metal alkoxide, as is often the case in the production of tin oxide gels since alkoxy groups readily undergo hydrolysis to give good quality

25   sols. Gels can be applied to a substrate by dipping or spin-coating techniques but are not particularly adaptable to aerosol applications in view of their inherent instability and particulate nature. For this reason, sol-gel techniques are suitable for fabricating small area films but are less useful for large scale industrial processes, such as film coatings for bottles and

30   domestic glass ware. Furthermore, sol-gel formation is generally a slow process.

The above methods are particularly disadvantageous in that they either require the use

of specialised equipment and environmentally unfriendly chemicals or are not suitable for large scale applications. It is the insoluble and intractable nature of most metal oxides and titanium oxides and tin oxides in particular which necessitate the use of these techniques for preparation of oxide coatings.

5

Aerosol and spin coating techniques do not suffer from the above disadvantages but these are most effective particularly the aerosol technique, when species are in the solution. There are more favourable techniques which do not have the above disadvantages however have been found to be unsuitable coating techniques for many metal oxides as they require the oxide to be soluble.

10

In the aerosol technique, a solution or gel is propelled under pressure through a fine nozzle thus producing a very fine aerosol. The fine aerosol may, for example, be directed onto the hot substrate such that instant evaporation of the solvent occurs to leave a uniform film of the oxide. Aerosol techniques are particularly suitable for large scale applications and work best when the material to be fabricated into the film is in solution. Another of these techniques is spin coating which requires the use of either a gel or a solution. In spin coating the gel or solution is applied to the substrate which is spun in a controlled manner such as to leave a uniform layer for subsequent processing stages and ultimate use. A metal oxide in solution would prove particularly advantageous for film fabrication since cheap and fast aerosol based techniques could be effectively employed for substrate coating. Alternatively spin coating techniques could be employed to produce films of uniform thickness.

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Thus any type of metal oxide which is suitable for use in these processes is advantageous.

PCT Publication No. WO 03/027191 discloses a curable liquid resin composition comprising a metal oxide, an organic compound, a compound having two or more polymerizable unsaturated groups in the molecule, a specific alkylene glycol organic solvent on the polymerization initiator.

30

European Patent Application No. 00956908.8 discloses an organic solvent based

dispersion of conductive powder and conductive coating material comprising conductive tin oxide particles coated with an organic metal coupling agent on the surface of the tin oxide particles and a dispersant.

5   US Patent No. 6,399,688 discloses a coating composition comprising a metal oxide a hydrophilic binder, a colloidal silica and a solvent.

The disadvantage of the above compositions is that they are resins and dispersions containing metal oxides and are not soluble metal oxides or solutions thereof and are

10   therefore not suitable for coating techniques and other applications requiring solutions. Thus until now it has not been possible to obtain a solution comprising a metal oxide. Furthermore, it has not been previously possible to carry out further chemical procedures on metal oxide which can only be carried out using solutions.

15   **Statements of Invention**

According to the invention there is provided a soluble metal oxide comprising:

one or more metal oxide particles;

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an inner organic binding group attached to each metal oxide particle; and

an outer organic binding group attached to each inner organic binding group.

25   The advantage of having a soluble metal oxide is that it can be dissolved in a solvent to provide a solution. When in solution chemical modification of the metal oxide in the solution can be carried out in a controlled fashion. Furthermore the surfaces of a metal oxide when dissolved in a solution are more chemically active than when the metal oxide is in the form of a gel.

30
Furthermore these soluble metal oxides have excellent long term stability in solution. Solutions can be highly concentrated or very dilute such that high quality thin and thick oxide films can be applied to a substrate using spin coating or aerosol techniques (e.g. in the glass industry). Additionally, due to the enhanced surface activity and chemical

reactivity of the metal oxides in solution they can be usefully employed to produce doped and conducting metal oxide films for the electronics industry and gas sensor devices, for a range of applications. The solubility of the metal oxide opens new routes to the development of metal oxide coatings exhibiting controlled drug release such as are sought after by the biomedical industry. The metal oxide solutions also introduce many new possibilities for the development of mixed metal oxide catalysts and immobilised catalysts (catalysts attached to the oxide surface). The metal oxides in solution can also be easily applied to fabrics allowing the fabric to act as both a fire retardant and mordent for dyeing applications.

The metal oxide in solution has the potential of mimicking or indeed outperforming the catalytic activity and roles of organo stannoxane systems and thus dispensing with the use of the latter. In the case of tin oxide, the availability of tin oxide solutions presents unforeseen possibilities for the development of tin oxide based catalysts. These may be of the mixed metal oxide type (e.g. tin/vanadium or tin/copper oxides) or surface bound catalysts, such as chiral oxidation catalysts which are extremely valuable in the pharmaceutical industry and may be immobilised on the tin oxide surface with relative ease and in high concentration when the oxide is in solution. Since it is now becoming increasingly clear that tin oxide is a biocompatible material the tin oxide solutions provide valuable new possibilities for the fabrication of tin oxide surfaces with drug retention and controlled release capabilities. Additionally, with the ability to bring tin oxide specifically into solution, a new route exists in the separation of tin oxide from other interfering oxides in the tin refining industry.

In one embodiment of the invention

each inner organic binding group is attached to each metal oxide particle by a covalent bond; and

each outer organic binding group is attached to each inner organic binding group by a hydrogen bond.

The advantage of having inner and outer organic binding groups is that it allows

increased solubility of the metal oxide particles in the organic solvent. The inner organic binding groups directly bonded to the metal oxide do not themselves give rise to solubility. They are however required since their presence is absolutely essential for the attachment of the outer organic binding group in sufficient quantity to the metal

5   oxides. The outer organic binding groups control solubility of the metal oxide.

In one embodiment of the invention

the outer organic binding group is a caboxylate group of the formula

10

$CR_2 R' COOH$

wherein R=R'=H or F; R=H; R' =CH_3

15   Preferably the weight of the outer organic binding group is approximately one quarter of the weight of the metal oxide particles. The advantage of this weight is that it allows solubility of the metal oxide particles.

Ideally, the outer organic binding group is selected from the group comprising one of

20   acetate; fluoroacetate; propionate; phosphate and phenylphosphonate.

Ideally each metal oxide particle has a particle size in the range 15Å-25Å. The advantage of the metal oxide particles having a particle size in the range 15Å-20Å is that as the particle size of the metal oxide particles are very small, the surface area is

25   very large. This is advantageous as it enhances reactivity with the organic binding groups.

Preferably the metal oxide is selected from the group comprising one of tin oxide and titanium oxide.

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According to the invention there is further provided a metal oxide solution comprising the soluble metal oxide and a solvent selected from the group comprising one of acetic acid; methanol; tetrahydrofuran; acetone; dimethyl-formamide; pyridine; ethanol and water.

According to the invention there is further provided a process for preparing a soluble metal oxide comprising:

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        drying hydrous metal oxide at a temperature in the range 20°C to 30°C until a powder is formed;

        adding an amount of the dried hydrous metal oxide in the range 2g to 55g to

10

        $100cm^3$ of acid to provide a metal oxide suspension;

        heating the suspension at a temperature of at least 70°C for 30 mins;

        removing the acid at a pressure of less than 25mm.Hg to provide the soluble

15

        metal oxide

The advantage of the metal oxide being hydrous is that there are water and hydroxyl molecules surrounding the metal oxide particles, which can be substituted easily by organic binding groups, which can then bind to the metal oxide particles.

20

Ideally the acid is a glacial acid. The advantage of the acid being a glacial acid is that it contains less than 1% water. As water will impede the interaction between the acid and the metal oxide it is advantageous to have minimal water bound to the acid. Water can successfully replace all organic binding groups bound to the metal and thus

25

its presence should be kept to a minimal level.

Preferably the acid is an organic acid. The advantage of the acid being an organic acid is that other types of acids do not interact in the same way with the metal oxides. For example mineral acids such as nitric acid are not suitable because the oxide

30

breaks down, and an oxide solution is not formed.

Further preferably the acid is selected from the group comprising one of methanoic acid; acetic acid; propanoic acid; and trifluoroacetic acid. The advantage of using these acids is that their removal at high temperatures as required in forming metal

oxide film does not leave groups that would introduce undesirable impurities into the metal oxide.

The advantage of heating the suspension to a temperature of at least 70°C is that it facilitates a fast exchange reaction between the hydroxy groups of the hydrous metal oxide and the organic binding groups of the acid so as to bond a sufficient percentage of organic binding groups to the metal oxide particles.

The advantage of removing the acid at a pressure less than 25mm.Hg is that it facilitates the fast removal of acid without any significant loss of organic binding groups.

According to the invention there is provided a process for modifying the solubility of a soluble metal oxide comprising:

heating the soluble metal oxide to a temperature in excess of 250°C to provide insoluble metal oxide;

adding an amount of the insoluble metal oxide in the range 1g to 15g to 50cm^3 of acid to provide a metal oxide suspension;

heating the metal oxide suspension to a temperature in excess of 70°C for 10 mins;

removing the acid to provide a soluble metal oxide.

According to the invention there is further provided a process for modifying the solubility of a soluble metal oxide comprising:

adding the soluble tin oxide in the range 1.5g to 3.0g to an amount of methanol in the range 30cm^3 to 100cm^3;

adding acid dropwise;

removing the methanol.

Preferably the acid is selected from the group comprising one of phosphoric acid and phenylphosphonic acid.

In one embodiment of the invention the acid is replaced with 8-hydroxyquinoline.

The advantage of adding a small quantity of an acid such as phosphoric acid is that good solubility in water can be achieved. The small quantity of phosphate introduced can have the effect of delaying particle size growth at high temperatures. Furthermore, small quantities of phosphate in a tin oxide can enhance catalytic performance. The presence of phosphate does not detract from biocompatibility. A tin oxide film on a hip-replacement joint greatly reduces the coefficient of friction, which is most desirable and the presence of phosphate introduces an element of compatibility with the bone structure.

Detailed Description of the Invention

The invention will be more clearly understood from the following description of some embodiments thereof given by way of example only and with reference to the accompanying drawings wherein:

Fig. 1 is a process outline for the preparation of a soluble metal oxide.

Fig. 2 illustrates powder diffraction patterns of hydrous insoluble tin oxide (lower) and soluble tin oxide (upper).

Fig. 3 illustrates powder diffraction patterns of hydrous insoluble tin oxide (a) and soluble tin oxide (b) at temperatures of 200°C, 400°C, 600°C, 800°C and 900°C.

Fig. 4 illustrates thermograms of hydrous insoluble tin oxide (b) and soluble tin oxide (a).

Fig. 5 illustrates the infrared spectra of soluble tin oxide.

According to Fig. 1 there is provided a process for the production of a soluble metal oxide.

In step 1 hydrous metal oxide is obtained and is dried at room temperature until it crumbles into a powder in step 2. In step 3, an amount of the dried hydrous metal oxide in the range 2g to 55g is added to a $100cm^3$ glacial acid to form a metal oxide suspension. In step 4 the metal oxide suspension is heated to a temperature of at least 70°C and is maintained at this temperature for at least 30 mins to form a solution. The solution is filtered to remove any undissolved material in step 5. In step 6, the glacial organic acid is removed under a reduced pressure of less than 25mm.Hg to provide the soluble metal oxide in step 7.

Obviously filtering is an optional step which is only carried out if necessary.

The hydrous metal oxide may be obtained commercially and can also be prepared by hydrolysis of a metal tetrachloride or metal alkoxide. A typical process for the preparation of hydrous tin by hydrolysis of tin tetrachloride is as follows. Tin tetrachloride (20 cm.^{3}) was added to water (200 cm.^{3}) to give a highly acidic solution. The pH of this solution was slowly raised to 6 after which the hydrous tin oxide was removed by centrifuging the solution. The very fine white solid was washed 8 times with distilled water to effect the total removal of chloride. Following a final washing with acetone, to speed the drying process, the solid was left to dry in the open atmosphere at room temperature. Approximately 10.5 g. of dry hydrous tin oxide was obtained by this process. This oxide is insoluble in all organic solvents and in water.

Example 1: Preparation of a Soluble Tin Oxide Suitable using Acetic acid

Preparation

Insoluble hydrous tin oxide was obtained and dried at room temperature until the tin

oxide crumbled into a powder. 10.5g of the dried insoluble hydrous tin oxide was added to $100cm^3$ of glacial acetic acid to provide a tin oxide suspension. The suspension was stirred for one hour at room temperature. No apparent dissolution of the insoluble tin oxide was noted. The tin oxide suspension was heated to a

5   temperature of approximately 85°C and at this temperature the oxide was slowly consumed into the solution. When the temperature approached 100°C the solids had completely disappeared giving a clear solution. Heating was discontinued and the solution was filtered. The acetic acid was removed using an evaporating apparatus such as a Rotavap™ at a pressure of 17mm.Hg provided by a water pump. The

10 remaining white solid was the soluble tin oxide.

Analysis

Analysis of the soluble tin oxide showed that it had a carbon content of approximately

15 9-10% and an acetate content in the region of 22-24%. The carbon content was measured using a carbon, nitrogen, hydrogen analyser and the amount of carbon correlates to the amount of acetate present.
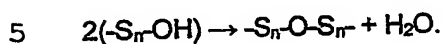
The soluble tin oxide was found to be soluble in cold glacial acetic acid and cold

20 methanol. It was found that approximately 1000g of soluble tin oxide could be dissolved in 1 litre of methanol at room temperature to give a clear transparent solution. The soluble tin oxide was also found to have some solubility in ethanol and water.

25 **X-ray Powder Diffractometry Studies**

Powder diffraction patterns of hydrous insoluble tin oxide, and soluble tin oxide are shown in Fig. 2. The patterns are essentially identical. The average particle size of the insoluble tin oxide and soluble tin oxide was calculated to be 19Å.

30
Samples of both insoluble tin oxide and soluble tin oxide were heated to temperatures of 200°C, 400°C, 600°C, 800°C and 900°C. At each of these temperatures powder diffraction patterns and infrared spectra were recorded. The diffraction patterns are indicated in Fig. 3. As the temperature was raised sintering occurred (i.e. an increase

in particle size with increasing temperature) to give large crystallites, this is indicated by a narrowing of the diffraction lines. Sintering also results in the loss of water molecules and due to the reaction denoted by the following formula:

5      $2(-Sn-OH) \rightarrow -Sn-O-Sn- + H_2O$.

The response of the oxides to heating was found to be essentially identical except at 400°C where the diffraction lines of soluble tin oxide were found to be broader than those of insoluble tin oxide, thus indicating that at this temperature a slight retardation 10   of the sintering process occurs as a result of the presence of the acetate groups.

Thermogravimetric Analysis

A number of soluble tin oxide samples were prepared as above and thermograms for 15   each of the samples were recorded. These thermograms showed consistency both in terms of thermogram form and in terms of quantitative weight losses over the temperature range. Typical thermograms of both insoluble tin oxide and soluble tin oxide are shown in Fig. 4. The thermogram for insoluble tin oxide is typical to that recorded by many authors and shows the greatest weight loss occurring up to a 20   temperature of approximately 120°C and tailing off with increasing temperature beyond this point. In contrast, the thermogram for the soluble tin oxide shows three well defined areas of weight loss in each of which there is a linear relationship between the weight loss and temperature. There was found to be a steep weight loss with increasing temperature in the range 25-100°C and this was followed by a tailing off into 25   a second region extending to approximately 300°C. The slope of the line in this region is very much less than that in the lower temperature region. Finally, a further marked increase in weight loss with increasing temperature occurred in the approximate region 300-450°C. No further significant weight loss beyond this point was recorded.

30   The weight loss of the soluble tin oxide would appear to correspond to the loss of acetate groups. The sharp loss of weight in the region 300 – 450 ° C is due to the most tightly bound acetate. Tin acetates, in which acetate is coordinated to tin, show acetate weight loss in this area and thus it can be assumed that for soluble tin oxide this is also weight loss due to acetate bonded to tin, an assumption which

is supported by infrared data.

Infrared Spectra

5   The infrared spectra of soluble tin oxide are indicated in Fig. 5. The infrared spectra of soluble tin oxide at room temperature show a very broad absorption in the region 1,450-1,650cm^{-1}: This is a general region where the acetate υ(C-O)$_{asym}$ is observed. A much sharper band appeared at 1350 cm.$^{-1}$ and is attributable to the acetate υ(C-O)$_{sym}$ related vibration. This latter band always displays shouldering on the high

10   frequency side. A sharp band is always observed at 1710 cm.$^{-1}$. It has been found that this band results from acetic acid forming a hydrogen bond to acetate bonded to tin. Significantly, the band diminishes with increasing temperature and samples heated to 300°.C no longer display this band. This is consistent with the thermogravimetric studies which indicate that the loss of weight up to 300° C is

15   associated with acetate not bound directly to tin. The absorption in the region 1450 – 1650 cm.$^{-1}$ of the spectrum of the sample heated to 300° C must result from acetate bonded to tin. The broadness of the absorption undoubtedly points to the presence of more than one type of tin bound acetate and this is further supported by the pronounced shoulder on the band attributable to υ(C-O)$_{sym}$ at 1350 cm.$^{-1}$.

20.

When acetate is bonded to tin through one of its oxygen atoms (i.e. unidentate acetate) as, for example, in K$_2$[Sn(acetate)$_6$] υ(C-O)$_{asym}$ is observed in the approximate region 1630 - 1675 cm.$^{-1}$ region while υ(C-O)$_{sym}$ is observed above 1300 - 1340 cm. $^{-1}$ region. On the other hand, when acetate is bonded through

25   both its oxygen atoms (i.e. bidentate acetate), υ(C-O)$_{asym}$ is observed close to 1560 cm.$^{-1}$, while υ(C-O)$_{sym}$ is observed at a frequency close to 1400 cm.$^{-1}$. Thus, the spectrum of soluble tin oxide that has been heated to 300° C shows extremely clear evidence for the presence of both unidentate and bidentate acetates bonded to tin.

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A Theoretical Model of a Soluble Tin Oxide Crystallite

The data from thermal, diffraction and spectroscopic data can be combined to postulate a model of a soluble tin oxide crystallite structure.

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It would appear that the X-ray diffraction data point consistently to an average particle size of 19 Å. Considering that tin oxide crystallises in the tetragonal system with the unit cell parameters a = 4.737 Å and b = 3.186 Å, a good model for the crystallite is a 5 x 5 x 5 block of unit cell giving an average core crystallite

10 size of 19.8 Å. On the assumption that the (1,0,0), (0,1,0) and (0,0,1) faces dominate the surface of the crystallite, the total number of tin atoms is 341 and the number of surface tins is 152. The ratio of surface to total tins is 2.24.

If the final loss of weight in the thermograms (i.e. in the 300 – 350 $^\circ$ C range) is

15 due entirely to loss of acetate, the ratio of tin bound acetate to total tin varies in the range 2.3:1 to 2.7:1 and thus practically all surface tins have an associated bound acetate. The model also gives the number of free hydroxyl groups on the surface as 264. If each of the 152 surface tins has an associated acetate group, acetate groups replace 152 hydroxyls. 112 hydroxyl groups remain and these

20 produce 56 molecules of water over the temperature range of the thermogravimetric studies. Thus, knowing the weight of tin bound acetate that is lost, the weight of a molar equivalent of water can be calculated and if this is scaled by the factor 56/152 the weight loss due to hydroxyl group conversion to water is obtained. This always works out to be close to 6% of the total weight loss.

25

Calculations indicate that by changing the nature of the crystal planes bounding the crystallites, the above general situation will not be significantly altered. Thus, approximately 88% of weight loss registered by the thermograms is due to acetate and approximately 6% weight loss. is a result of the sintering process. There

30 remains a small weight loss, approximately 6% due to hydrogen bonded water.

Example 2: Preparation of Soluble Tin Oxide using Trifluoroacetic acid

Preparation

5   Insoluble hydrous tin oxide was obtained and dried at room temperature as described previously. 5g of the dried insoluble hydrous tin oxide was added to $10cm^3$ of trifluoroacetic acid to provide a tin oxide suspension. The suspension was heated to 70°C and it was noted that the hydrous tin oxide was completely dissolved to give a clear solution. The trifluoroacetic acid was removed on a Rotovap™ to leave a white

10   powder of the soluble tin oxide.

Analysis

15   The carbon content of the soluble tin oxide was found to be in the range 6-6.5%, and the soluble tin oxide was found to have a fluoroacetate content in the range 18.26% to 30.61%.

Solubility

20

The soluble tin oxide was found to be soluble in methanol, acetone and tetrahydrofuran. For example, the solubility in both acetone and tetrahydrofuran was found to be greater than 1000 g per litre of solvent.

25   **X-Ray Powder Diffractometry**

The room temperature powder diffraction pattern is identical to that of the soluble tin oxide of example 1 and particle size, as measured from line width analysis, indicate average particle size of approximately 19 Å. In other words, average

30   particle size is similar to that for the soluble tin oxide which was prepared using acetic acid. Studies of diffraction data for samples heated to various temperatures up to 900° C indicated that while particle size increases with increasing temperature (sintering process), this increase is not as great as for soluble tin oxide prepared from the acetic acid process.

Infrared Spectroscopy

Where bands associated with υ(C-O)$_{asym.}$ occur in the region 1600 – 1750 cm.$^{-1}$, the spectrum of soluble tin oxide exhibits a broad absorption centred at 1696 cm.$^{-1}$. However, this band has a number of very well defined shoulders to higher and lower frequencies thus indicating different roles of the trifluoroacetate groups. When the sample is heated to 300° C, all but those trifluoroacetate groups which are bound to the tin are removed and the infrared spectrum of this heated sample shows a less complicated spectrum in the 1600 – 1750 cm.$^{-1}$ range; two broad overlapping peaks centred at 1640, and 1672 cm.$^{-1}$. In the 1400 cm.$^{-1}$ region where bands associated with υ(C-O)$_{sym.}$ occur, a broad weak absorption occurs. The broadness of this band suggests the presence of more than one band. Likewise, two strong bands associated with CF$_3$ rocking occur at 1199 and 1152 cm.$^{-1}$. Thus, the infrared data point to two types of trifluoroacetate bound directly to tin (as is the case for acetate in soluble tin oxide obtained from the acetic acid process).

Example 3: Preparation of a Soluble Tin Oxide using Propanoic Acid

Preparation

The method of preparation of the soluble tin oxide is directly analogous to that for the process for preparation using acetic acid (Example 1), except that acetic acid is replaced with propanoic acid.

Analysis

Analysis of the soluble tin oxide confirmed the presence of propanoic acid groups. The carbon content was found to be in the range in the range 12 – 13% and the soluble tin oxide was found to have a propionate content in the range 24.35% to 26.38%. When this form of soluble tin oxide is heated under vacuum for one hour at 100° C, the carbon content reduced to approximately 10.5 %, and the propionate content reduced to 21.3%.

Solubility

Soluble tin oxide prepared by this process was found to be soluble in
tetrahydrofuran, methanol and in dimethyl-formamide. It was also found to have
some solubility in pyridine. Samples heated to $100°$ C under vacuum retained their
solubility.

Thermogravimetric Data

Thermograms of this form of soluble tin oxide bear all the characteristics of the
soluble tin oxides prepared using acetic acid.

Powder Diffractometry

The powder diffraction pattern of this form of soluble tin oxide is identical to that of
the soluble tin oxides prepared using acetic acid revealing a particle size of
approximately 19 Å. In the sintering process the powder diffraction patterns reveal
that this form of soluble tin oxide behaves essentially identically to the soluble tin
oxides prepared using acetic acid

Infrared Spectra

In the important regions $1500 - 1750$ cm.$^{-1}$ and $1300 - 1450$ cm.$^{-1}$ the spectra are
better defined than those for the soluble tin oxides prepared using acetic acid. Two
bands at 1564 and 1623 cm.$^{-1}$ are attributable to $\upsilon(C-O)_{asym}$, while a band at 1376
cm.$^{-1}$ and at approximately 1420 cm.$^{-1}$ (appearing as a clearly defined shoulder)
are attributable to $\upsilon(C-O)_{sym}$. These bands are consistent with the presence of
monodentate and bidentate propionate groups bound to tin. A sharp band
appearing at 1716 cm.$^{-1}$ is attributable to hydrogen bonded propanoic acid
molecules. Thus, on the basis of both the thermogravimetric and infrared data, it
would appear that the roles of propionate parallel those of acetate in the soluble
tin oxides prepared using acetic acid

Example 4: Preparation of a Soluble Titanium Oxide using Acetic acid

Preparation

5   Insoluble hydrous titanium oxide was obtained and dried at room temperature until it crumbled into a powder. 6g of the dried insoluble hydrous titanium oxide was added to 200cm^3 of glacial acetic acid to provide a titanium oxide suspension. The suspension was heated to the boiling point of glacial acetic acid at a temperature in the region of 119°C and maintained at this temperature for 3 hours. The titanium oxide did not

10   dissolve and was subsequently removed by filtration and dried in air. The remaining acetic acid filtrate was removed using a Rotovap™ to leave a small quantity of white solid. The X-ray powder diffraction pattern indicated that it is not an oxide. This insoluble titanium oxide/acetate material was added to glacial acetic acid and the suspension was maintained at boiling point for 3 hours. The solid was isolated by

15   filtration and dried in air. The acetic acid filtrate in this case was found not to contain any dissolved material.

All of the insoluble material from the above process was added to 200cm^3 methanol and a large excess of 8-hydroxyquinoline was added. A yellow colour immediately

20   was observed in the solution and the solid also assumed a yellow colour. After refluxing for 4 hours the solution had assumed a deep yellow colour, as also had the undissolved material. The solution was filtered and the methanol of the filtrate was removed on a Rotovap to leave a yellow powder. This powder was repeatedly washed with diethylether and finally allowed to dry at room temperature. An infrared spectrum

25   of this yellow material confirmed the presence of bound 8-hydroxyquinoline and the absence of unreacted 8-hydroxyquinoline. Its X-ray powder diffraction pattern confirmed that the material was a titanium oxide. This form of titanium oxide is highly soluble in methanol. Solubility is retained, albeit reduced, in samples heated to 300°C. The soluble oxide sintering process was monitored by X-ray diffraction. It parallels the

30   behaviour of hydrous titanium oxide and in the sintering process the yellow colour changes to a red colour and finally the material becomes colourless at 800°C.

Analysis

Analysis of the soluble titanium oxide showed that it had a carbon content of approximately 2-8% and an acetate content in the region of 4.92% to 19.68%.

Example 5: Control of solubility of the metal oxide by surface group removal and replacement

The outer organic binding group which is bound to the metal oxide confers solubility to the metal oxide. The organic binding group depends on the acid used to prepare the soluble metal oxide. Thus when acetic acid is used the organic binding group is an acetate, when trifluoroacetic acid is used the organic binding group is a fluoroacetate group, and when propanoic acid is used, the organic binding group is a propionate group. As discussed in the previous examples the different organic binding groups confer different levels of solubility to the metal oxide in different solvents.

It is further possible to modify the type of solubility of each soluble metal oxide.

(a)   **Modification of acetate bound soluble tin oxide to provide fluoroacetate bound soluble tin oxide**

Soluble tin oxide having acetate groups as organic binding groups was prepared as in Example 1. 2g of the soluble tin oxide was heated to 300°C, at which temperature it became insoluble. The insoluble tin oxide was added to 10cm^3 trifluoroacetic acid and the suspension was heated to 100°C. After 10 minutes at this temperature, the material was totally dissolved to give a clear solution. The trifluoroacetic acid was removed by a Rotovap™ to give a soluble tin oxide that now had solubility in methanol, tetrahydrofuran and acetone. In other words, the material now behaved like soluble tin oxide prepared using trifluoroacetic acid.

(b)   **Modification of fluoroacetate bound soluble tin oxide to provide acetate bound soluble tin oxide**

2g of soluble tin oxide having fluoroacetate groups as organic binding groups was prepared as in Example 2 and was heated to 300°C at which temperature

it became insoluble. The insoluble tin oxide was added to 50cm^3 acetic acid and the suspension was heated to 100°C. After 10 minutes at this temperature, the material was totally dissolved to give a clear solution. The acetic acid was removed by a Rotovap™ to give a soluble tin oxide that was soluble in methanol but not tetrahydrofuran or acetone. In other words, the soluble tin oxide now had the solubility characteristics of soluble tin oxide prepared using acetic acid.

(c) **Modification of acetate bound soluble tin oxide to provide propionate bound soluble tin oxide**

2g of soluble tin oxide having acetate groups as organic binding groups was prepared as in Example 1 and was heated to 300°C at which temperature it now became insoluble. The insoluble tin oxide was added to 50cm^3 propanoic acid and the suspension was heated to 120°C. After 10 minutes at this temperature, the material was totally dissolved to give a clear solution. The propanoic acid was removed using a Rotovap™ to give a soluble tin oxide that was soluble in methanol, tetrahydrofuran and acetone. In other words, the soluble tin oxide now had the solubility characteristics of soluble tin oxide prepared using propanoic acid.

(d) **Modification of acetate bound soluble tin oxide to provide phosphate bound soluble tin oxide**

2g soluble tin oxide having acetate groups as organic binding groups was prepared as in Example 1 and dissolved in 30cm^3 of methanol. Concentrated phosphoric acid was slowly added at room temperature and the resulting solution stirred at room temperature for 10 minutes. The molar quantity of phosphoric acid was confined to be in the region of 100th of the molar quantity of tin present. The methanol was removed on a Rotovap™ to leave a colourless material. The infrared spectrum of this material confirmed the presence of both acetate and phosphate; not free phosphoric acid. An X-ray powder diffraction of the material confirmed the retention of the tin oxide rutile structure. This material had excellent solubility in methanol (similar to that of the soluble tin oxide prepared using acetic acid) but furthermore, it also had excellent solubility in water. The phosphate-modified material gave perfectly

stable aqueous solutions.

(e) **Modification of acetate bound soluble tin oxide to provide phenylphosphonate bound soluble tin oxide.**

2g soluble tin oxide having acetate groups as organic binding groups was prepared as in Example 1 and was dissolved in 40cm^3 of methanol. Phenylphosphonic acid dissolved in 10cm^3 methanol was added drop wise to the soluble tin oxide – methanol solution over a period of 10 minutes (the tin:phenylphosphonic acid molar ratio was 10:1). After stirring for a half hour at room temperature, the methanol was removed by a Rotovap™. The remaining white solid was repeatedly washed with acetone to remove unreacted phenylphosphonic acid. The infrared spectrum of the washed white material showed the presence of both phenylphosphonate and acetate and further confirmed the absence of unreacted phenylphosphonic acid. A powder diffraction pattern confirmed the retention of the tin oxide rutile structure. This form of soluble tin oxide has very good solubility in methanol.

(f) **Modification of acetate bound soluble tin oxide to provide 8-hydroxyquinoline bound soluble tin oxide**

2g soluble tin oxide having acetate groups as organic binding groups was prepared as in Example 1 and was dissolved in 100cm^3 of methanol. Solid 8-hydroxyquinoline was added in large excess to give a bright yellow solution. After stirring for a half hour at room temperature, the methanol was removed by a Rotovap™. The remaining yellow solid was repeatedly washed with diethylether to remove unreacted 8-hydroxyquinoline. The diethylether contained unreacted 8-hydroxyquinoline. The infrared spectrum of the washed yellow material showed the presence of both bound 8-hydroxyquinoline and acetate and further confirmed the absence of unreacted 8-hydroxyquinoline. A powder diffraction pattern confirmed the retention of the tin oxide rutile structure. This form of yellow soluble tin oxide has very good solubility in methanol.

In the specification the terms "comprise, comprises, comprised and comprising" or any variation thereof and the terms "include, includes, included and including" or any

variation thereof are considered to be totally interchangeable and they should all be afforded the widest possible interpretation and vice versa.

The invention is not limited to the embodiments hereinbefore described but may be varied in both construction and detail.
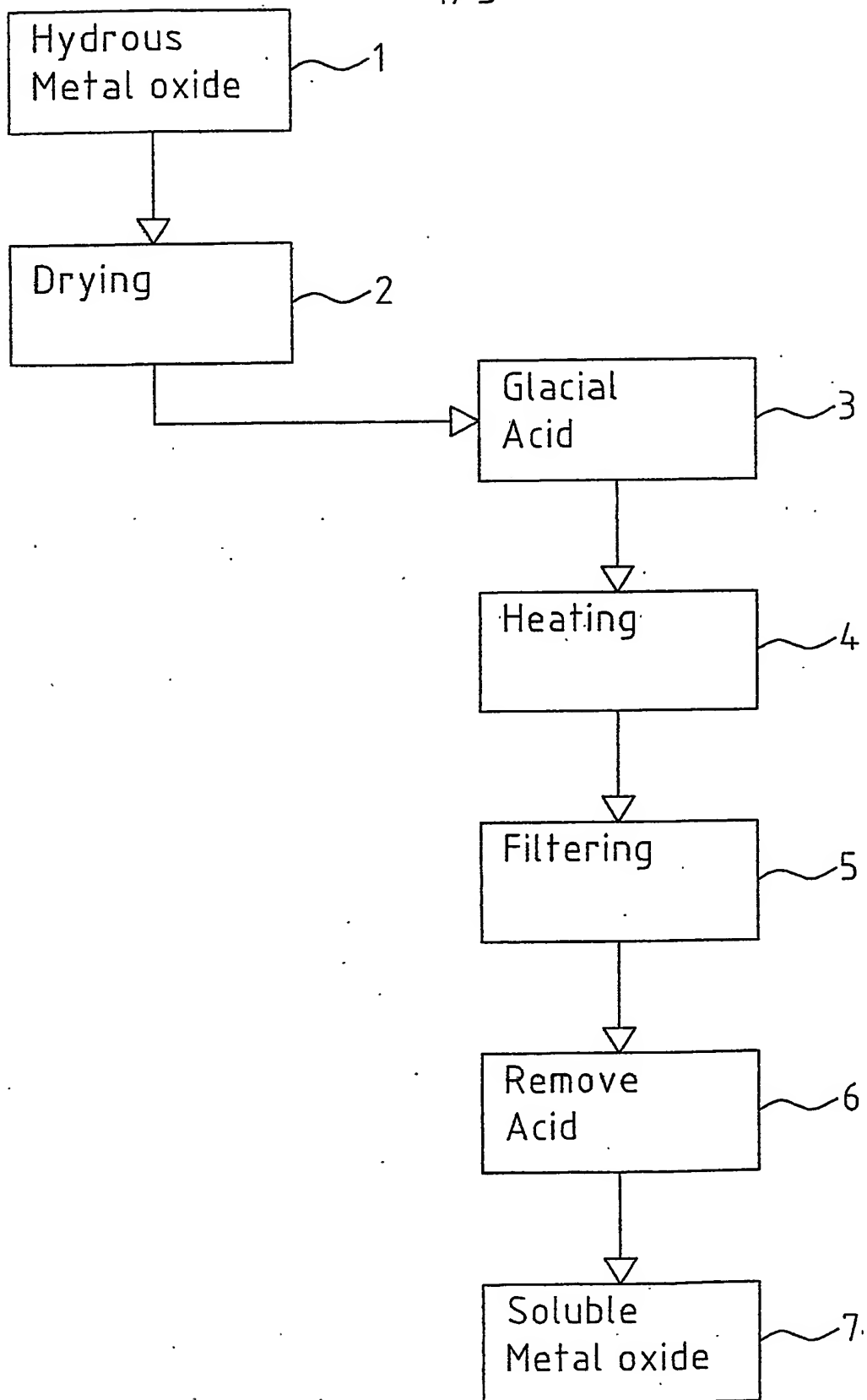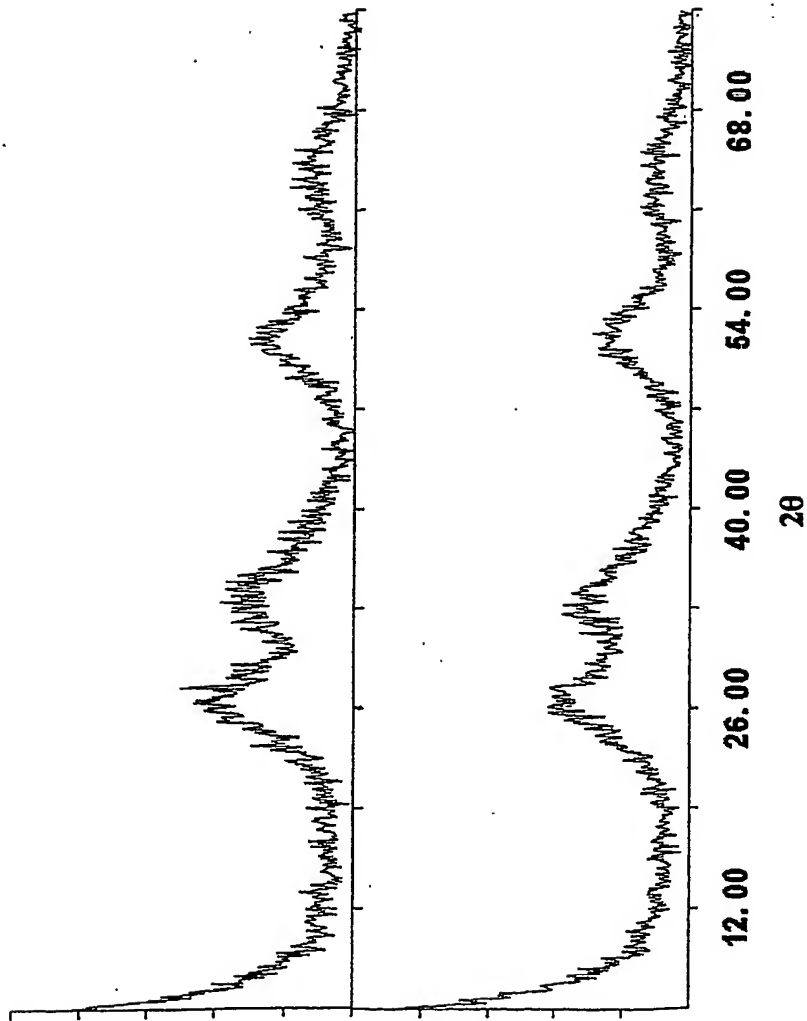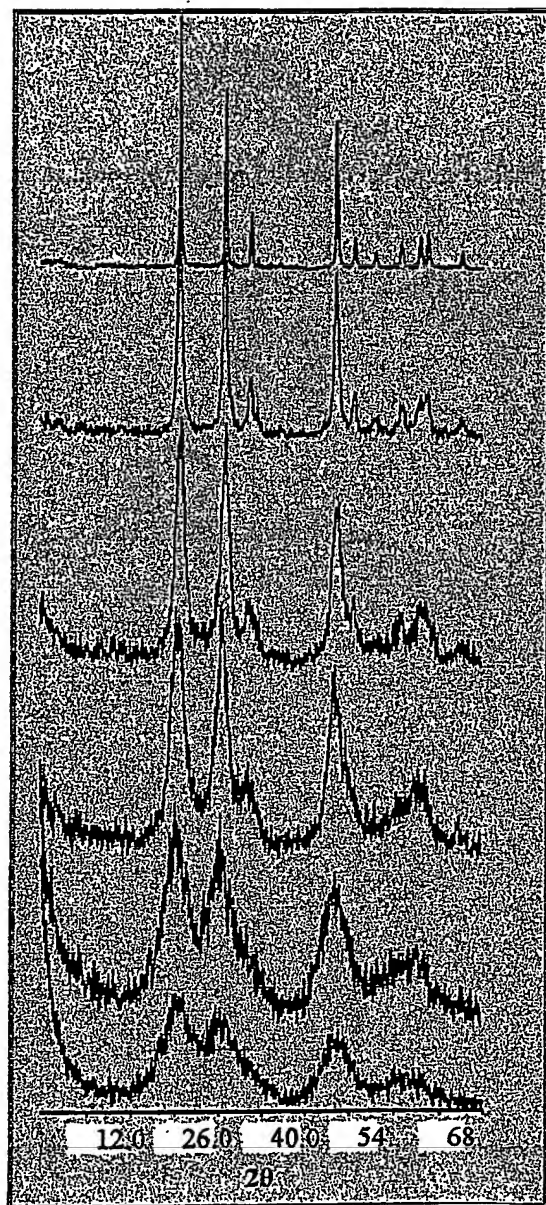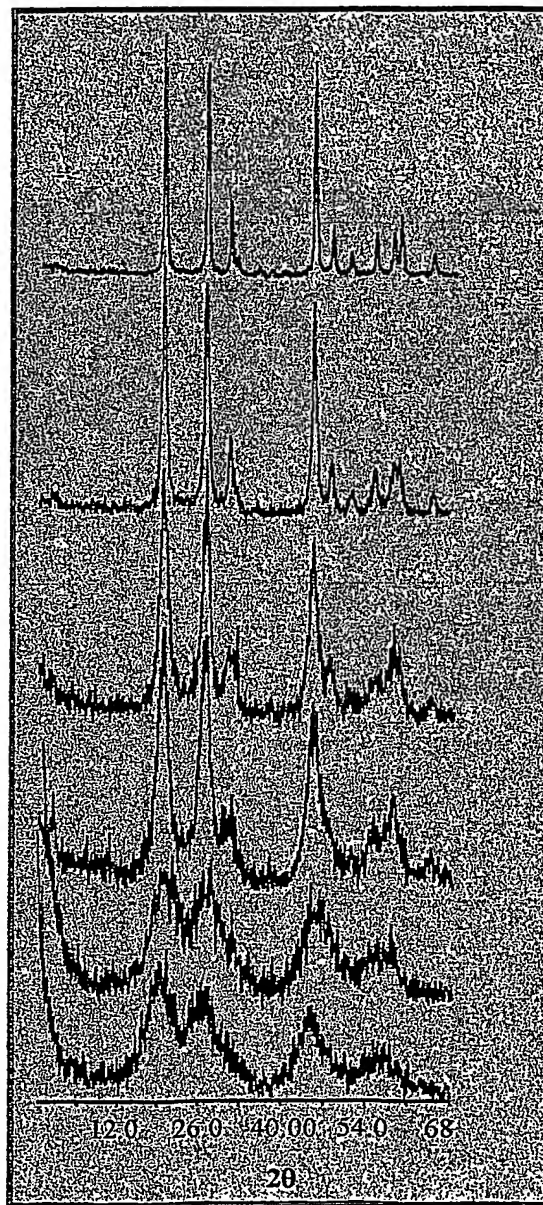
Hydrous
Metal oxide — 1

↓

Drying — 2

Glacial
Acid — 3

↓

Heating — 4

↓

Filtering — 5

↓

Remove
Acid — 6

↓

Soluble
Metal oxide — 7

Fig. 1

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Fig. 2

(a)

(b)

<u>Fig. 3</u>

(a)

(b)

Fig. 4

Fig. 5